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Title of the Invention: Separator for Capacitors

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Applicant: Nitto Electric Industrial Co., Ltd.

Inventors: T. Hiyui and T. Murakami

[CLAIM]

A separator for capacitors, comprising a laminate obtained by laminating a porous polymer material on the following polymer membrane (A):

(A) a polymer membrane comprising a fluorine-base porous polymer membrane impregnated with a fluorine-base surface active agent making use of the pores of the membrane.

[DETAILED DESCRIPTION OF THE INVENTION]

[Field of Utilization in Industry]

The present invention relates to a separator suitable for capacitors, for example, a separator for an electrolytic capacitor or an electric double-layer capacitor, having sufficiently high affinity for the electrolytic solution, having heat resistance stably for a long period of time and having excellent rolling up workability of the separator during the production process of a capacitor.

[Prior Art]

The separator for capacitors hitherto used include a paper-made base material such as kraft paper and Manila paper, and a polyethylene-made or polypropylene-made porous membrane subjected to graft polymerization of a hydrophilic monomer. A porous membrane obtained by treating a fluoro-resin with an alcohol (Japanese Unexamined Patent Publication (Kokai) No. 62-263624) and a fluoro-resin porous membrane covered with a substance having affinity for a polar organic solvent (Japanese Unexamined Patent Publication (Kokai) No. 2-241013) have also been proposed. Further, a hydrophilized membrane

obtained by impregnating a fluorine-base surface active agent into a fluoro-resin porous membrane and cross-linking the membrane to fix (Japanese Examined Patent Publication (Kokoku) Nos. 5-21009 and 5-21010) has been proposed.

[Problems to be Solved by the Invention]

However, these techniques are disadvantageous in that the kraft paper or Manila paper is deteriorated when it is subjected to a high temperature in an electrolytic solution or cannot be used because it becomes fragile in an acidic electrolytic solution such as sulfuric acid. The polyethylene-made or polypropylene-made porous membrane is inferior in the heat resistance and therefore, on use for a long period of time at a high temperature or short-time heating at 200°C or higher during the production process of a capacitor, the membrane is melted and the holes are clogged. The porous membrane obtained by treating a fluoro-resin with an alcohol is reduced in the amount of solution absorbed due to drying of the membrane during the long-term use. In the case of the fluoro-resin porous membrane covered with a specific perfluoro-ion exchange polymer as a substance having affinity for a polar organic solvent, the polymer has only one  $-CF_3$  terminal as the hydrophobic moiety and is weak in the affinity for the membrane, accordingly, depending on the polymer selected, sufficiently high hydrophilic property cannot be achieved and the separator obtained is far from the satisfactory level. In the case of the hydrophilized membrane obtained by impregnating a fluorine-base surface active agent into a fluoro-resin porous membrane and cross-linking the membrane to fix, the porous membrane is soft and therefore, even after impregnation of a fluorine-base surface active agent into the porous membrane and fixing of the membrane by cross-linking, the nerve is still insufficient, as a result, wrinkles are readily generated during the production process of a capacitor and the workability is very bad.

The present invention has been made under these

circumstances and the object of the present invention is to provide a separator for capacitors, having excellent heat resistance, sufficiently high affinity for the electrolytic solution and superior workability in the production process of capacitors.

[Means to Solve the Problems]

In order to attain the above-described object, the separator for capacitors of the present invention has a structure such that the separator comprises a laminate obtained by laminating a porous polymer material on the following polymer membrane (A):

(A) a polymer membrane comprising a fluorine-base porous polymer membrane impregnated with a fluorine-base surface active agent making use of the pores of the membrane.

[Mode of Operation]

The present inventors have made a series of studies so as to obtain a separator having heat resistance, sufficiently high affinity for the electrolytic solution and superior workability free from generation of wrinkles or the like during the production process of a capacitor. As a result, they have found that when a laminate comprising a polymer membrane (A) impregnated with a fluorine-base surface active agent making use the pores thereof and having laminated thereon a porous polymer material is used as the fluorine-base porous polymer membrane, since the polymer membrane (A) has both heat resistance and affinity for an electrolytic solution and the porous polymer material offers reinforcing action, the capacitor using this separator can have desired capacitor characteristics and at the same time, since wrinkles or the like are not generated at the production process of a capacitor, the workability can be improved.

The present invention is described in detail below.

The separator for capacitors of the present invention comprises a laminate obtained from a porous polymer material and the above-described specific polymer membrane (A).

The material for forming the porous polymer material is not particularly limited and those not having reactivity with the electrolytic solution and having appropriate rigidity are preferred. Examples thereof include polyethylene, polypropylene, polyimide, polyether sulfone, polyether ketone, polyether ether ketone, nylon, polystyrene and polyurethane. A mixture or copolymer of these resins may also be used.

The porous shape thereof is also not particularly restricted and any shape may be used as long as the ions in the electrolytic solution can freely move in or out. Examples of the shape include non-woven fabric, woven fabric, net (meshed sheet) and porous membrane each made of the material described above. The materials having these shapes may be used as a single layer or may be used as a laminate of two or more layers. The porous polymer material preferably has a pore size of from 0.01  $\mu\text{m}$  to 20 mm, more preferably from 0.1  $\mu\text{m}$  to 5 mm.

The above-described specific polymer membrane (A) is a polymer membrane (A) obtained by impregnating a fluorine-base porous polymer membrane with a fluorine-base surface active agent making use of the pores of the membrane.

Examples of the fluorine-base porous polymer membrane include hydrophobic porous membranes comprising polytetrafluoroethylene (PTFE), tetrafluoroethylene-perfluoroalkylvinyl ether copolymer (PFA), tetrafluoroethylene-hexafluoropropylene copolymer (FEP), ethylene-tetrafluoroethylene copolymer (ETFE) or polychlorotrifluoroethylene (PCTFE). In view of the chemical resistance and heat resistance, PTFE is preferred. The membrane preferably has a pore size of from 0.01 to 20  $\mu\text{m}$ , more preferably from 0.05 to 5  $\mu\text{m}$ .

Examples of the fluorine-base surface active agent which is impregnated into the above-described fluorine-base porous polymer membrane making use of the pores thereof include (a) anionic, (b) cationic and (c) nonionic fluorine-base surface active agents described below. These surface active agents are used individually or in combination of two or more thereof. From the standpoint that the membrane is used as a

separator for capacitors, a metal-free fluorine-base surface active agent is preferably used.

Examples of (a) the anionic fluorine-base surface active agent include perfluoroalkyl carboxylate, perfluoroalkyl sulfonate and perfluoroalkyl phosphate, and examples of the positive component for forming these salts include  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Li}^+$  and  $\text{NH}_4^+$ . The perfluoroalkyl group preferably has from 4 to 20 carbon atoms.

Examples of (b) the cationic fluorine-base surface active agent include perfluoroalkyl quaternary ammonium salts such as perfluoroalkyltrimethyl ammonium salt, and examples of the negative component for forming these salts include  $\text{Cl}^-$  and  $\text{NO}_3^-$ . The perfluoroalkyl group preferably has from 4 to 20 carbon atoms.

Examples of (c) the nonionic fluorine-base surface active agent include a perfluoroalkylethylene oxide adduct and a perfluoroalkylamine oxide adduct represented by the following formulae (1) and (2), respectively. The perfluoroalkyl group in the perfluoroalkylamine oxide adduct preferably has from 4 to 20 carbon atoms.

[Chemical 1]



(wherein  $4 \leq m \leq 20$  and  $5 \leq n \leq 20$ .)



(wherein  $\text{R}_1$ ,  $\text{R}_2$  and  $\text{R}_3$ , which may be the same or different, each is  $-\text{H}$ ,  $-\text{OH}$ ,  $-\text{COOH}$  or  $-\text{CH}_3$ ,  $4 \leq p \leq 20$  and  $1 \leq q \leq 20$ ).

The method for impregnating a fluorine-base surface active agent into the micropores of the fluorine-base porous polymer membrane is not particularly limited, however, for example, a method of diluting the above-described fluorine-base surface active agent with an organic solvent to from 0.2 to 10% by weight (hereinafter simply referred to as "%"), preferably from 1 to 5%, and immersing a fluorine-base porous polymer membrane in the fluorine-base surface active agent solution, or a method of coating the solution and drying the

membrane may be used. The organic solvent for use in the dilution is not particularly limited, however, suitable examples thereof include acetone, ethanol and isopropyl alcohol.

A coating layer comprising the fluorine-base surface active agent is formed by the above-described method at least on the micropore surface of the fluorine-base porous polymer membrane. Thus, a porous membrane rendered to have affinity for the electrolytic solution can be easily obtained. The term "micropore surface" as used herein means the surface of fiber constituting the pore. It is sufficient if the coating layer is formed on the micropore surface, namely, in the inside of the polymer membrane in the thickness direction. The coating layer may also be formed on the surface of the above-described porous polymer membrane.

The extent in the formation of the coating layer formed by the impregnation of the fluorine-base surface active agent can be appropriately controlled by the concentration of the fluorine-base surface active agent, the immersion time or the amount coated, however, for using this as a constituent element of the separator of the present invention, the weight ratio between before and after the coating (after formation of the coating layer/before formation of the coating layer) is preferably from 1.040/1 to 1.070/1, more preferably from 1.045/1 to 1.060/1. Based on the weight before formation of the coating layer, if the weight after formation of the coating layer is less than 1.040, sufficiently high affinity for the electrolytic solution cannot be obtained, whereas if it exceeds 1.070, the amount of the coating layer to come off after the formation of the coating layer increases and the capacitor characteristics (e.g., tangent of loss angle, impedance) are liable to deteriorate.

The production method of the separator for capacitors of the present invention is not particularly limited, however, for example, it can be produced as follows. A coating layer comprising the fluorine-base surface active agent is formed on the micropore surface of the fluorine-base porous polymer

membrane by the above-described method to prepare the polymer membrane (A). Then, a porous polymer material is welded to the polymer membrane (A). Or, an adhesive layer is formed on the porous polymer material surface and the polymer membrane (A) may be laminated and bonded onto the adhesive layer surface to integrate the members.

Examples of the material for forming the adhesive layer include an ionic conductive adhesive. By coating an adhesive, the adhesive layer is formed. The adhesive is used for integrating the polymer membrane (A) and the porous polymer material in the production process of capacitors and when rolling up of the electrode foil and the separator is completed in the production process of a capacitor using the separator for capacitors of the present invention, the adhesive may dissolve in the electrolytic solution injected thereafter and lose the adhesive function. Accordingly, the ion conductivity as described above is another characteristic required for the ion conductive adhesive. Specific examples of the ion conductive adhesive include polyvinyl alcohol (PVA), starch, carboxymethyl cellulose (CMC), polyethylene oxide (PEO), polyvinylpyrrolidone (PNVP) and polyacrylic acid (PAA). These adhesives may be used individually or in combination of two or more thereof.

The thus-produced separator for capacitors is a laminate having a multi-layer structure comprising a polymer membrane (A) and a porous polymer material. In the present invention, the separator is not limited to the two-layer structure, but three-layer or greater multi-layer structure may be formed using a plurality of polymer membranes (A) or a plurality of porous polymer materials. In this case, the lamination order is not particularly limited. For example, in order to obtain a more nerved separator, a laminate using a plurality of porous polymer materials may be prepared.

The laminate is not limited to the laminate of the polymer membrane (A) and the porous polymer material, but a paper-made base material such as Manila paper may also be used or a non-woven reinforcing member may be formed directly on

the polymer membrane (A) by melt blowing, so that the same effect as in the laminate of the polymer membrane with the porous polymer material can be obtained.

Examples of the capacitor using the separator for capacitors of the present invention include an electrolytic capacitor where the separator is impregnated with an electrolytic solution and disposed between a pair of electrodes, and an electric double-layer capacitor. Examples of the electrolytic solution for use in the electrolytic capacitor include those containing an electrolyte such as adipate or phthalate, in a solvent such as ethylene glycol,  $\gamma$ -butyrolactone or dimethylformamide (DMF). The electrodes used are an anode foil and a cathode foil. Examples of the anode foil include those obtained by forming a dielectric film on the surface of a metal foil having a film forming capability, such as aluminum and tantalum, through anodization or the like. Examples of the cathode foil include the same metal foils as those for the anode foil. The metal foil is preferably subjected to etching so as to increase the surface area per the volume.

Examples of the electrolytic solution for use in the electric double-layer capacitor include an aqueous solution-type electrolytic solution using an aqueous sulfuric acid solution and an aqueous potassium hydroxide solution, and a non-aqueous solution-type electrolytic solution obtained by dissolving an electrolyte such as perchlorate of alkylammonium, in an organic solvent such as  $\gamma$ -butyrolactone, dimethylformamide, dimethyl sulfoxide or propylene carbonate. The electrode is not particularly limited, however, examples thereof include activated carbon fiber cloth and activated carbon fiber cloth having formed on one surface thereof an electrically conductive layer.

#### [Effects of the Invention]

As described in the foregoing, the separator for capacitors of the present invention comprises a laminate obtained by laminating a porous polymer material on the



specific polymer membrane (A). As having such a construction, excellent heat resistance and sufficiently high affinity for the electrolytic solution owing to the polymer membrane (A) are imparted, the nerve is intensified owing to the porous polymer material, thereby wrinkles or the like are not generated in the production process of capacitors, and the production workability is improved. By using this separator, the quality of the capacitor and the production efficiency can be improved.

The present invention is described below by referring to the Examples and Comparative Examples.

In advance of the experiments, three kinds of fluorine-base surface active agents shown in Table 1 below were prepared.

[Table 1]

|                             | Fluorine-base Surface Active Agent             |   |                                 |
|-----------------------------|--|---|---------------------------------|
|                             | a  | b   | c                               |
| Ionicity                    | anionic  | cationic                                      | nonionic                        |
| Appellation                 | perfluoroalkyl carbonate                       | perfluoroalkyl trimethylammonium salt         | perfluoroethylene oxide adduct  |
| Kind of salt                | sodium   | nitrate                                       | none                            |
| Manufacturer and trade name | Dainippon Ink & Chemicals, Inc., Megafac F-120 | Dainippon Ink & Chemicals Inc., Megafac F-150 | Daikin Kogyo KK, Unidyne DS-403 |

[Example 1]

A 15  $\mu\text{m}$ -thick PTFE-made porous membrane (NTF-1033, produced by Nitto Electric Industrial Co., Ltd., pore size: 3  $\mu\text{m}$ ) was immersed in an isopropyl alcohol solution having a weight concentration of 3% and having dissolved therein an anionic fluorine-base surface active agent a (shown in Table 1) for 10 minutes, then pulled up and dried at 40°C for 30 minutes to obtain a polymer membrane having impregnated into the micropores thereof the fluorine-base surface active agent (the weight ratio between before and after the immersion,

after immersion/before immersion = 1.050/1). Separately, a polypropylene-made net (XN3301, manufactured by Conwed, fiber diameter: 70  $\mu\text{m}$ , basis weight: 5  $\text{g}/\text{m}^2$ , opening: 3.5 mm) was prepared and welded on the surface of the polymer membrane prepared above at 180°C to obtain a desired separator for capacitors.

[Example 2]

A 15  $\mu\text{m}$ -thick PTFE-made porous membrane (NTF-1033, produced by Nitto Electric Industrial Co., Ltd., pore size: 3  $\mu\text{m}$ ) was immersed in an isopropyl alcohol solution having a weight concentration of 3% and having dissolved therein an anionic fluorine-base surface active agent a (shown in Table 1) for 10 minutes, then pulled up and dried at 40°C for 30 minutes to obtain a polymer membrane having impregnated into the micropores thereof the fluorine-base surface active agent (the weight ratio between before and after the immersion, after immersion/before immersion = 1.050/1). Separately, an aramid non-woven fabric (MXX<sub>200</sub>, produced by Nippon Ferrite Kogyo KK, thickness: 42  $\mu\text{m}$ , METSUKU: 20  $\text{g}/\text{m}^2$ , fiber diameter: 20  $\mu\text{m}$ ) was prepared and bonded to the surface of the polymer membrane prepared above through a polyvinyl alcohol (adhesive) layer to obtain a desired separator for capacitors.

[Comparative Example 1]

A 15  $\mu\text{m}$ -thick PTFE-made porous membrane (NTF-1033, produced by Nitto Electric Industrial Co., Ltd., pore size: 3  $\mu\text{m}$ ) was immersed in an isopropyl alcohol solution having a weight concentration of 2% and having dissolved therein an anionic fluorine-base surface active agent a (shown in Table 1) for 10 minutes, then pulled up and dried at 40°C for 30 minutes to obtain a polymer membrane having impregnated into the micropores thereof the fluorine-base surface active agent (the weight ratio between before and after the immersion, after immersion/before immersion = 1.050/1).

[Example 3]

A 15  $\mu\text{m}$ -thick PTFE-made porous membrane (NTF-1033, produced by Nitto Electric Industrial Co., Ltd., pore size: 3  $\mu\text{m}$ ) was immersed in an isopropyl alcohol solution having a weight concentration of 3% and having dissolved therein an anionic fluorine-base surface active agent b (shown in Table 1) for 10 minutes, then pulled up and dried at 40°C for 30 minutes to obtain a polymer membrane having impregnated into the micropores thereof the fluorine-base surface active agent (the weight ratio between before and after the immersion, after immersion/before immersion = 1.050/1). Separately, a polypropylene-made net (XN3301, manufactured by Conwed, fiber diameter: 70  $\mu\text{m}$ , basis weight: 5 g/m<sup>2</sup>, opening: 3.5 mm) was prepared and welded on the surface of the polymer membrane prepared above at 180°C to obtain a desired separator for capacitors.

[Example 4]

A 15  $\mu\text{m}$ -thick PTFE-made porous membrane (NTF-1033, produced by Nitto Electric Industrial Co., Ltd., pore size: 3  $\mu\text{m}$ ) was immersed in an isopropyl alcohol solution having a weight concentration of 3% and having dissolved therein an anionic fluorine-base surface active agent c (shown in Table 1) for 10 minutes, then pulled up and dried at 40°C for 30 minutes to obtain a polymer membrane having impregnated into the micropores thereof the fluorine-base surface active agent (the weight ratio between before and after the immersion, after immersion/before immersion = 1.050/1). Separately, a polypropylene-made net (XN3301, manufactured by Conwed, fiber diameter: 70  $\mu\text{m}$ , basis weight: 5 g/m<sup>2</sup>, opening: 3.5 mm) was prepared and welded on the surface of the polymer membrane prepared above at 180°C to obtain a desired separator for capacitors.

The thus-obtained separators for capacitors of the Examples and Comparative Examples each was interposed between two electrode foils of an anode foil and a cathode foil.

Then, as shown in Fig. 1, the members were rolled up into a cylindrical form and lead wires 3 were connected to anode foil 1 and cathode foil 2, respectively, to prepare a capacitor device 4. In Fig. 1, 7 is the separator. Thereafter, as shown in Fig. 2, the capacitor device 4 was loaded into an aluminum case 8 to prepare an electrolytic capacitor. At this time, whether or not the wrinkles or the like were generated during the preparation process of the electrolytic capacitors using a separator of Examples 1 to 4 and Comparative Example was visually observed. 100 capacitors were produced per each separator and those having no generation of wrinkles were counted. The results are shown in Table 2 below.

[Table 2]

|   | Examples |    |    |    | Comparative Example |
|---|----------|----|----|----|---------------------|
|   | 1        | 2  | 3  | 4  |                     |
| Number of good products free of wrinkles (per 100 products) | 98       | 98 | 98 | 99 | 10                  |

As is apparent from the results in Table 2, the products of the Comparative Example had generation of wrinkles at a ratio of 90%, whereas the products of the Examples all were prevented from generation of wrinkles on loading the separator during the production process of the capacitor and verified to have excellent rolling up workability at the preparation of capacitors.

#### [BRIEF DESCRIPTION OF DRAWINGS]

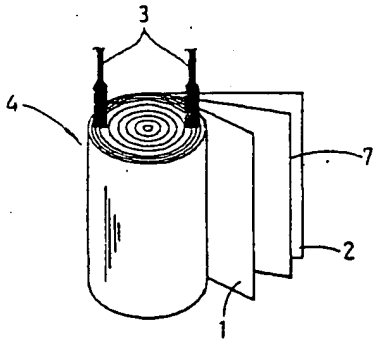
##### [FIG. 1]

Fig. 1 is a perspective view showing a capacitor device prepared by interposing a separator.

##### [Fig. 2]

Fig. 2 is a view showing the cross section of an electrolytic capacitor having loaded therein the capacitor of Fig. 1.

[FIG. 1]



[Fig. 2]

